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(54) Photolabile blocked surfactants and compositions containing the same.

(57) Surfactants which are blocked against surfactant action (identified herein as "photolabile blocked surfactants") by a photolabile protective or masking group but which, on exposure to actinic radiation, become unblocked are provided. Coating compositions in which surfactant is formed on irradiation are provided by blending the photolabile blocked surfactant with polymeric film-forming materials.

Compositions containing the photolabile blocked surfactants are useful when employed as protective coatings on various substrates or as the adhesive in a pressure sensitive adhesive tape. Although initially well adhering to a substrate, such compositions may be readily removed from the substrate following exposure of the same to suitable radiation which unblocks the surfactant to permit it to regain its surfactant activity.

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DescriptionPhotolabile Blocked Surfactants and
Compositions Containing the SameTechnical Field

5 This invention relates to surfactants which are blocked against surfactant activity and which are capable of regaining surfactant activity upon exposure to actinic radiation, to coating compositions containing the same, and to substrates coated with such compositions.

10 Background Art

 Many articles in the chemical literature discuss the use of photolabile groups to block (specifically to protect) a particular functional group, such as the carboxylic acid group, e.g., during synthesis involving poly-
15 functional molecules. In a review entitled Photosensitive Protecting Groups, Amit et al, Israel J. of Chem. 12 (1-2), 103-113 (1974) discuss the chemistry of photolabile protecting groups for carboxylic acids and give a large list of supporting references. None of these references, how-
20 ever, teach the blocking of surfactants by photolabile groups.

 Coating compositions suitable for providing substrates such as polished sheet material, machinery, molded articles and the like with a protective film or
25 coating that can be cleanly and inexpensively removed have been investigated for many years. Much of this investigation has been directed to adhesives for use on tapes or papers that can be applied to the substrate and peeled off cleanly when desired. These tapes and papers generally tend
30 to age with time so that, when removed, adhesive residues likely will remain on the surface of the substrate. Such tapes and papers are many times also unsatisfactory for use on substrates other than flat surfaces. Protective compositions which can be applied by brush, spraying or the like

and removed when desired by a solvent, preferably water, have also been described. The use of such compositions for protection of substrates is less than desirable because of untidy, often hazardous and corrosive conditions arising
5 from the use of solvents to remove the coating.

Disclosure of Invention

The present invention provides novel photolabile blocked surfactants, compositions comprising the photolabile blocked surfactants; e.g., a coating composition in
10 which surfactant is formed upon exposure to suitable radiation, and substrates bearing coatings of such compositions. The novel photolabile blocked surfactants of the invention are surfactants (i.e., compounds characterized by having a hydrophobic group and at least one polar hydro-
15 philic group) having their polar group(s) masked by a covalently bonded photolabile masking group. Because of the photolabile mask, the masked surfactant has substantially reduced surfactant activity as compared to the same surfactant in the unmasked state and, on exposure to
20 suitable radiation, the mask is removed, substantially restoring the surfactant to its original surface activity.

Specifically, the photolabile surfactant compounds of the invention have the general formula $(P-X)_aR$ wherein $(-X)_aR$ is the hydrogen-eliminated residue of a surfactant
25 having the formula $(H-X)_aR$ including the polar divalent radical X, P is a covalently bonded photolabile masking group which prior to exposure to actinic radiation masks the polar properties of X and upon exposure to actinic radiation will unmask the polar properties of X, and R is a hydro-
30 phobic group which provides in the surfactant $(H-X)_aR$ a log (critical micelle concentration, hereinafter designated "CMC") equal to or less than -2 and "a" is a number from 1 to 4 to satisfy the valency of R.

The coating composition comprises an actinic
35 radiation-transmissive film-forming binder which has blended

therein a photolabile blocked surfactant compound having the general formula $(P-X)_aR$, as defined above, in a quantity, functionally stated, sufficient to cause an appreciable change in the surface characteristics of the coating composition, i.e., a change in wettability or adhesion, upon exposure to actinic radiation. A preferred embodiment of the composition is of use in coatings which upon radiation are made releasable from the substrate.

A simple infrared spectroscopic analysis technique may be employed to identify the suitable photolabile covalently bonded blocked surfactants of the present invention. In this technique, a small amount (e.g., about 10-100 mg) of the test photolabile blocked surfactant (as a thin liquid film or as a mull in mineral oil) is analyzed to obtain an infrared spectrum. The sample is thereafter exposed to an ultraviolet source (e.g., using an H3T7 lamp from a distance of 3 cm) for a brief length of time and a second IR spectrum is obtained of the UV exposed sample. Useful compounds will show a change in the infrared spectrum due to breaking of the covalent bond and liberation of the polar group of the unblocked surfactant after UV light exposure. The UV light exposure time needed to cause this change will generally depend on several factors including the photosensitivity of the test compound, film thickness, etc. Generally, exposures of from 5 to 50 minutes will be sufficient and 15-30 minute exposures are more common.

Coated substrates according to the invention are provided by any of a variety of substrates coated with the coating composition described above.

Best Mode for Carrying Out the Invention

The surfactants constituting the novel photolabile blocked surfactants of the invention are those surfactants which, in their salt form, are commonly known as ionic surfactants. Suitable ionic surfactants are those having one or more salt forming polar group including carboxylic, sulfonic, phosphonic, phosphinic, sulfinic, amino and the like polar groups.

Suitable photolabile masking groups for use in the photolabile blocked surfactants (sometimes referred to as photoactivatable release agents) of the invention are any of the photolabile masking groups (often termed protecting groups) recognized in organic chemistry, particularly the chemistry of aminoacids, that can be covalently bonded to the polar groups (see previously cited review). Examples of such protecting groups include 2-nitrobenzyl, phenacyl, 2-nitroanilino, 2,4-dinitrobenzene-sulfonyl, 2-(2-azidoaryl)ether, 7-nitroindolino, β -nitrocinnamyl, and 8-nitrotetrahydroquinolino groups that can be substituted by one or more auxochromic or bathochromic groups.

Preferred photolabile blocked surfactants of the invention include those of the formula $(P-X)_a R$ wherein

P is as defined above; and

X is a polar group selected from $-OC(=O)-$, $-OS(=O)-$ and

-N- wherein R^1 is selected from hydrogen and lower alkyl
 $\begin{array}{c} | \\ R^1 \end{array}$

having one to four carbon atoms;

R is selected from:

(a) R^2-

5 (b) $R^3-\overset{\overset{O}{\parallel}}{C}-CH_2CH_2-$

(c) $R^3-\overset{\overset{O}{\parallel}}{C}-\underset{\underset{R^1}{|}}{N}(CH_2)_n$

(d) $R^4-O-\overset{\overset{O}{\parallel}}{C}-CH_2CH-\underset{\underset{R^4-OC=O}{|}}{CH_2}$

wherein R^2 is

10 (1) straight chain alkyl, alkenyl, alkynyl, or alkylphenyl group having 12 to 30 carbon

atoms when X is $-\overset{\overset{O}{\parallel}}{S}-$;

(2) straight chain alky, alkenyl, alkynyl, or alkylphenyl group having 15 to 30 carbon

atoms when X is $-\overset{\overset{O}{\parallel}}{C}-$ or $-\underset{\underset{R^1}{|}}{N}-$ in which R^1 is

15 defined above; or

(3) a perfluoroalkyl -alkenyl, or -alkynyl group having 7 to 30 carbon atoms;

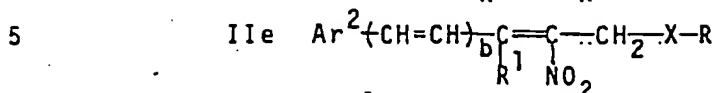
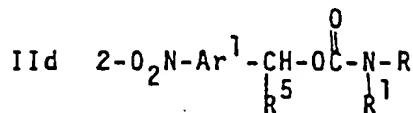
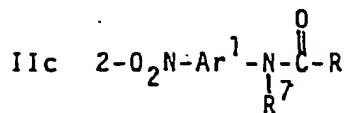
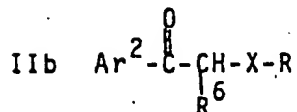
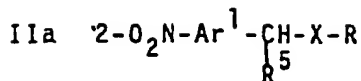
20 R^3 is a straight chain alkyl, alkenyl, alkynyl, or alkylphenyl group having 11 to 30 carbon atoms or a perfluoroalkyl group having 7 to 30 carbon atoms;

R^4 is a straight chain alkyl, alkenyl, alkynyl, alkylphenyl or perfluoroalkyl -alkenyl, or -alkynyl group having 7 to 30 carbon atoms;

n is 1 or 2; and

25 a is 1.

The most preferred photolabile blocked surfactants of the invention have the general formulae:



wherein X, R and R¹ are as defined above;

Ar¹ is a mononuclear or polynuclear divalent aryl group having 6 to 14 carbon atoms or heteroaromatic group having 5 to 13 carbon atoms with heteroatoms selected from oxygen, nitrogen or sulfur atoms, the nuclei of which may be substituted by one or more auxochromic or bathochromic groups, examples of which include nitro, chloro, bromo, phenyl, lower alkyl, lower alkoxy, lower thioalkoxy, amino, lower alkyl or dialkylamino, and the like groups and the aryl group Ar¹ may be the aryl group in a polymer; Ar² is preferably the same as Ar¹ except that Ar² is monovalent;

R⁵ is preferably hydrogen but may be lower alkyl or phenyl which may also be substituted by an auxochromic or bathochromic group as defined for Ar¹ or a lower alkylene group joining CH to Ar and forming a five- or six-membered heterocyclic ring;

R⁶ is preferably phenyl substituted by 3-alkoxy or 3,5-dialkoxy in which the alkyl group has 1 to 4 carbon atoms but can be a hydrogen atom, a lower alkyl group, e.g., having from 1-4 carbon atoms, or a phenyl group;

R⁷ can be hydrogen but preferably is lower alkyl having 1 to 4 carbon atoms or most preferably is lower alkylene having 2 to 4 carbon atoms joining N to Ar² forming five- or six-membered heterocyclic ring; and

b is zero or one.

Examples of specific preferred photolabile blocked surfactants of the invention include:

I Ia Compounds

- 5 2-Nitrobenzyl tetradecanesulfonate
2-Nitrobenzyl hexadecanesulfonate
2-Nitrobenzyl heptadecanoate
2-Nitrobenzyl hexadecanoate
4,5-Dimethoxy-2-nitrobenzyl octadecanoate
2-Nitrobenzyl 9-octadecenoate
10 2-Nitrobenzyl octadecanoate
2-Nitrobenzyl 4-dodecylbenzenesulfonate
4,5-Dimethoxy-2-nitrobenzyl hexadecanoate
4,5-Methylenedioxy-2-nitrobenzyl perfluorooctanoate
4,5-Methylenedioxy-2-nitrobenzyl bis(2-ethylhexyl)sulfosuccinate
15 4-Dimethylamino-2-nitrobenzyl N-octadecanoylsarcosinate
2,4-Dinitrobenzyl N-(“cocoyl”)taurate
3,4,5-Trimethoxy-2-nitrobenzyl hexadecanesulfonate
4,5-Dimethoxy-2-nitrobenzyl perfluorooctanoate
2-Nitrobenzyl N-octadecanoylsarcosinate
20 2-Nitrobenzyl tetraeicosanoate
2-Nitrobenzyl perfluorooctanoate
4,5-Dimethoxy-2-nitrobenzyl hexadecanesulfonate
N-(2-Nitrobenzyl)perfluorooctylamine
N-(2-Nitrobenzyl)octadecylamine
25 1-Nitronaphth-2-ylmethyl perfluorooctanoate
10-Nitro-1,2,3,4-tetrahydronaphth-1-yl perfluorooctanoate
7-Nitroindan-1-yl perfluorooctanoate
4-Dimethylamino-2-nitrobenzyl perfluorooctanoate
N-Methyl-(2-nitrobenzyl) octadecylamine
30 2-Octadecanoylpropanoyl substituted polystyrene
2-Perfluorooctanoylacetyl substituted poly(styrene/butadiene)
Bis(2-Nitrobenzyl ester) of 9-octadecenoic acid dimer

I Ib Compounds

- 35 3'-Methoxybenzoin octadecanoate
3',5'-Dimethoxybenzoin perfluorooctanoate
3'-Methoxybenzoin hexadecanoate

- 3'-Methoxybenzoin perfluorooctanoate
 α -Methylphenacyl tetradecanesulfonate
 α -Methylphenacyl perfluorooctanoate
 α -Methylphenacyl hexadecanesulfonate
5 α -Methyl-4-nitrophenacyl perfluorooctanoate
 α -Phenylphenacyl N-(octadecanoyl)taurate
 α -Phenylphenacyl pentadecylbenzenesulfonate
 α -(2,4-Dichlorophenyl)phenacyl bis(2-ethylhexyl)sulfosuccinate
Phenacyl octadecanoate
10 α -Methylphenacyl 14,14,14-trifluorohexadecanesulfonate
 α -Phenylphenacyl 1,1-difluorooctadecanoate
 α -n-Butylphenacyl octadecanoate
N-[α -(3-Methoxyphenyl)-4-chlorophenacyl]octadecenylamine
1-Indanon-2-yl perfluorooctanoate
15 3,4-Dihydro-1(2H)-naphthalenon-2-yl perfluorooctanoate
3'-Methoxybenzoin hexadecanesulfonate

Iic Compounds

- N-Perfluorooctanoyl-2-nitroaniline
N-Perfluorooctanoyl-N-methyl-2-nitroaniline
20 N-Octadecanoyl-2-nitroaniline
1-Perfluorooctanoyl-8-nitro-1,2,3,4-tetrahydroquinoline
N-Octadecanoyl-8-nitro-1,2,3,4-tetrahydroquinoline

IId Compounds

- N-Perfluorooctyl-0-(2-nitrobenzyl)carbamate
25 N-Hexadecyl-0-(2-nitrobenzyl)carbamate
N-Octadecyl-0-(2-nitrobenzyl)carbamate
N-Perfluorooctyl-0-(2-nitro-4-methoxybenzyl)carbamate
N-Octadecyl-0-(4,5-dimethoxyl-2-nitrobenzyl)carbamate

IIE Compounds

- 30 β -Nitrocinnamyl tetradecanesulfonate
 β -Nitrocinnamyl octadecanoate
 β -Nitrocinnamyl perfluorooctanoate
4-Methoxy- β -Nitrocinnamyl octadecanoate
5-Phenyl-2-nitro-1-octadecanoyloxypenta-2,4-diene

The compounds of general Formulae IIa, IIb, and IIc where X is $\begin{array}{c} \text{O} \\ \parallel \\ -\text{OC}- \end{array}$ or $\begin{array}{c} \text{O} \\ \parallel \\ -\text{OS}- \\ \parallel \\ \text{O} \end{array}$ are prepared from the corres-

ponding alcohol or halide and surfactant carboxylic or sulfonic acid or preferably acid chloride by conventional esterification procedures such as are described by Bottorff, U.S. Patent No. 3,745,188; Barltrop et al, Chemical Communications, 822 (1966); and Sheehan et al, J. Am. Chem. Soc. 86; 5277 (1964) and J. Org. Chem. 38 (21), 3771 (1973).

The compounds of general Formulae IIa and IIb where X is $\begin{array}{c} \text{N} \\ | \\ \text{R} \end{array}$ are prepared from the corresponding halide and surfactant amine in accordance with well known alkylation procedures. A preferred method for preparing the compounds of Formula IIa is to condense a nitrobenzaldehyde with a surfactant amine and reduce or reductively alkylate the Schiff's base obtained in accordance with well known methods to the desired blocked surfactant. The photosensitive 2-nitroarylamine amides of Formula IIc are prepared by acylation of o-nitroarylamines with surfactant carboxylic acid chlorides. The photosensitive carbamates of Formula IIId are prepared by conventional urethane reaction of the corresponding nitrobenzyl alcohol and a hydrophobic group-containing isocyanate such as perfluorooctylisocyanate, perfluorododecylisocyanate, hexadecylisocyanate, octadecylisocyanate and pentadecylphenylisocyanate.

Exemplary 2-nitrobenzyl alcohols of use for preparing photo-activatable surfactants of Formulae IIa and IIId include 2-nitrobenzyl, 2,4-dinitrobenzyl, 1-nitronaphthylmethyl, 4,5-dimethoxy-2-nitrobenzyl, 4,5-methylenedioxy-2-nitrobenzyl, 4-dimethylamino-2-nitrobenzyl, 4,5-dimethyl-2-nitrobenzyl, 4,5-dichloro-2-nitrobenzyl, 4-bromo-2-nitrobenzyl, 4-phenyl-2-nitrobenzyl, 4-methylthio-2-nitrobenzyl, 2-nitro- α -phenylbenzyl, bis(2-nitrophenyl)-methyl, 2-nitro- α -methylbenzyl, 2-nitro- α -n-butylbenzyl alcohol and the like. The corresponding chloride, bromide, and aldehydes of the aforementioned alcohols are suitable for

the preparation of the compounds of Formula IIa wherein X is -N-₁. The corresponding chlorides and bromides are

also useful for preparation of the compounds of Formula IIa

wherein X is $\begin{array}{c} \text{O} \\ \parallel \\ -\text{CO}- \end{array}$.

- 5 Exemplary phenacyl alcohols of use for preparing the blocked photoactivatable surfactant of Formula IIb include benzoin, α -methylphenacyl alcohol, 3'-methoxybenzoin, and 3',5'-dimethoxybenzoin and the corresponding halides.
- 10 Exemplary nitroarylamines of use for preparing the blocked photoactivatable surfactants of Formula IIc include 2-nitroaniline, N-methyl-2-nitroaniline, 8-nitro-1,2,3,4-tetrahydroquinoline, 4-chloro-2-nitroaniline, and 4-methoxy-2-nitroaniline.
- 15 Exemplary cinnamyl alcohols of use for preparing compounds of Formula Iie include β -nitrocinnamyl alcohol, 4-methoxy- β -nitrocinnamyl alcohol and 5-phenyl-2-nitropenta-2,4-dien-1-ol.
- 20 The film-forming binder component of the radiation activatable compositions of the invention are thermoplastic organic polymers preferably having a molecular weight of at least 10,000. Suitable polymers include:
- 25 (a) copolyesters based on terephthalic, isophthalic, sebacic, adipic and hexahydrophthalic acids such polyesters are sold under the trade designation "Vitel" by the Goodyear Tire and Rubber Company, (b) alkyd resins based on phthalic anhydride and glycerine available from Enterprise Paint Company under the trade designation "EPIC" Varnish. (c)
- 30 polyamides such as poly(hexamethyleneadipamide) and polycaprolactam, (d) vinyl acetate polymers such as that available under the trade designation "VINAC" ASB516 from Air Products Company and vinyl chloride copolymers such as the copolymer with vinyl acetate, e.g., those sold under the trade designation "VMCH", "VAGH", or "VYHH" by the
- 35 Union Carbide Company and under the trade designation "Geon" resin by the B.F. Goodrich Company, (e) vinylidene chloride copolymers, (f) ethylene copolymers, e.g., ethylene

or propylene and vinyl acetate, (g) polyacrylates such as polymethyl methacrylate and the copolymers of acrylic acid esters with other ethylenically unsaturated monomers, e.g., that sold under the trade designation "Carboset 525" by the B.F. Goodrich Company and methacrylate resins such as that sold under the trade designation "Elvacite" by the DuPont Company, the pressure sensitive adhesive copolymers of "soft" acrylic esters such as butyl or isooctyl acrylate and a "hard" monomer such as acrylic acid or acrylamide, (h) cellulose esters such as cellulose acetate/butyrate, (i) polyvinyl acetals such as polyvinyl butyral, (j) polyurethanes such as that sold by B.F. Goodrich Company under the trade designation "Estane 5715", (k) the polycarbonates, and (l) styrene-maleic anhydride or maleic acid copolymers

The radiation-releasable coating compositions of the invention may be prepared by mixing by any convenient method the film-forming binder and photolabile surfactant in a suitable solvent. Generally, from about one to about ten parts, preferably about two to five parts of photolabile surfactant are used per 100 parts of film-forming binder. Solutions are prepared to contain about 10 to 50 weight percent concentration of solids, the concentration used being that which provides a solution having a viscosity most suitable to the method by which the composition is to be applied to the substrate.

Solvents for use in the coating composition are chosen on the basis of film-forming binder. Suitable solvents include ketones such as acetone, methylethylketone, and methylisobutyl ketone; aromatic hydrocarbons such as benzene and toluene; halocarbons such as chloroform, methylene chloride, and trichloroethylene; esters such as ethyl acetate and propyl butyrate; ethers such as diethyl ether, dioxane, and tetrahydrofuran; nitromethane; nitroethane; and acetonitrile.

Various additives, such as coating aids, wetting agents, plasticizers, ultraviolet absorbers and dyes (as long as they do not absorb in the wavelength range of the photolabile release agent) can be added to the composition

in amounts and for purposes that are well known. Particulate material such as pigments, e.g., carbon black, clays titanium dioxide, umber, ochre and the like, microfibers, glass microspheres, alumina, etc., may also be added;

- 5 however, only small amounts, i.e., less than about 5%, can be tolerated since the surfactant liberated on irradiation will tend to orient about particulate material and be lost to orientation at the substrate surface.

10 The compositions are favorably used to provide substrates with a removable protective coating. Substrates that can be coated include metal, e.g., steel, nickel, aluminum; plastics, e.g., polyester, polyvinyl chloride, polyurethane, epoxy resins, phenol-formaldehyde resins, etc.; glass, ceramic and the like. The use of many primers
15 on substrates to improve adherence of the coating is not detrimental since the protective coatings of the invention are releasable on irradiation even when applied over primers.

The substrate can be coated by any of the
20 conventional means, including spray, brush, dip pad, roll-coating, curtain and knife techniques, and may, if desired, be dried under ambient or oven conditions to provide coating films on the substrate.

A typical example of the use of the removable
25 protective coatings of the invention is the use of the coating to protect a substrate against damage by abrasion during conditions such as shipment or a shaping operation, e.g., cutting. A composition of the invention is prepared, the substrate coated, and the coating dried. After the
30 shipment or shaping operation, when it is desired to remove the protective coating, it is subjected to radiation having wavelengths preferably in the range between about 200 and 400 nanometers. Radiation having wavelengths above 400 nm can also be used when the protective coating contains photo-
35 labile blocked surfactants having auxochromic groups that extend the absorption characteristics of the blocked surfactant into the visible range of radiation. Protective coatings having photolabile blocked surfactants absorbing

in the visible range are less desirable unless the protected substrate is to be manipulated in darkness since such coatings would have the tendency to release prematurely.

Suitable sources of radiation include carbon arcs, mercury vapor arcs, fluorescent lamps with ultraviolet radiation-emitting phosphors, argon and xenon glow lamps, and electronic flash units. Customarily, mercury-vapor arcs are used at a distance of 1 to 20 inches (2.5 to 50 cm) or more from the protective coating to bring about release. Radiation fluxes of 10 to 10,000 w/cm² are generally suitable for use.

The following examples will aid in further explaining, but should not be deemed as limiting, the instant invention. In all cases, unless otherwise noted, all parts and percentages are by weight.

PREPARATION OF PHOTOLABILE BLOCKED SURFACTANTS

Each of the photolabile blocked surfactants described herein is identified by a "Compound Number" which is used hereinafter to refer to the same.

20

EXAMPLE 1

2-Nitrobenzyl perfluorooctanoate (Compound 1)

Perfluorooctanoyl chloride (21.6 g, 0.05 mol) was added slowly with stirring to a solution of 2-nitrobenzyl alcohol (7.65 g, 0.05 mol) and triethylamine (5.2 g, 0.05 mol) in 100 ml benzene. During the addition, the temperature was allowed to rise to 50°C and the triethylamine hydrochloride began to precipitate. After the addition was complete, the reaction was stirred an additional 30 minutes. The reaction was filtered and the filtrate evaporated in vacuo to give an oil which crystallized on cooling in an ice bath (m.p. 34-35°C). Benzene washings of the material retained on the filter paper gave a second fraction of oil which crystallized on cooling. Total yield was 11.97 g.

30

EXAMPLE 2

35

α-Methylphenacyl perfluorooctanoate (Compound 2)

2-Bromopropiophenone (10.65 g, 0.05 mol) was added to a solution of perfluorooctanoic acid (20.7 g, 0.05

mol) and triethylamine (5.05 g, 0.05 mol) in 100 ml of DMF. The solution was stored at 0-2°C for three days, filtered to remove precipitated ammonium salt, and mixed with 700 ml of ice water. The oil which separated was collected and
5 crystallized from 95% ethanol to yield 6.2 g of the ester [IR 1775 cm^{-1} ; UV (ethanol) λ_{max} 244, 279 and 325 (sh) (nm)].

EXAMPLE 3

N-(2-Nitrobenzyl)octadecylamine (Compound 3)

Octadecylamine (13.5 g, 0.05 mol) was dissolved in
10 warm absolute ethanol (300 ml) and 2-nitrobenzyl chloride was added. After three days at room temperature, the mixture was cooled and the unreacted octadecylamine which crystallized was removed by filtration. The filtrate was evaporated to dryness and the residue dissolved in dilute aqueous hydro-
15 chloric acid. Ether extraction of the acidic solution removed unreacted 2-nitrobenzyl chloride. The aqueous layer was made basic with potassium hydroxide solution and the resulting mixture was extracted with ether. The dried ether layer was evaporated to yield an oil which crystallized. Crystalliz-
20 ation from methanol gave pure product (0.8 g, m.p. 53-56°C).

EXAMPLE 4

2-Nitrobenzyl octadecanoate (Compound 4)

In 100 ml benzene were mixed 2-nitrobenzyl alcohol (7.65 g, 0.05 mol) and triethylamine (5.06 g, 0.05 mol).
25 To the solution octadecanoyl chloride (15.14 g, 0.05 mol) was added dropwise with stirring. The mixture was stirred an additional one hour and the precipitated triethyl amine hydrochloride was removed by filtration. The filtrate was evaporated to dryness and the residue crystallized from
30 ethanol (yield 13.0 g, m.p. 60-61°C). The tetradecanoate (m.p. 46°C) (Compound 5), hexadecanoate (m.p. 54°C) (Compound 6), heptadecanoate (m.p. 48°C) (Compound 7), and 9-octadecanoate (Compound 8) esters of 2-nitrobenzyl alcohol were similarly prepared using corresponding acyl chlorides in
35 place of octadecanoyl chloride.

EXAMPLE 5

A. 2-Nitrobenzyl hexadecanesulfonate (Compound 9)

To a stirred solution of 7.65 g (0.05 mol) of 2-nitrobenzyl alcohol in 75 ml of benzene containing 5.05 g

(0.05 mol) of triethylamine was added 16.25 g (0.05 mol) of hexadecanesulfonyl chloride. The mixture was stirred an additional four hours. The mixture was evaporated to dryness in vacuo and the solid taken up into a mixture of
5 ether and water. The ether layer was separated and dried over $MgSO_4$. Evaporation of the ether gave a solid which was crystallized from absolute ethanol (yield 14.3 g, m.p. 63-65°C),

B. 4,5-Dimethoxy-2-nitrobenzyl hexadecanesulfonate (Compound 10)

10. To a solution of 5.33 g (0.025 mol) of 4,5-dimethoxy-2-nitrobenzyl alcohol and 8.15 g (0.025 mol) hexadecanesulfonyl chloride in 100 ml of acetone, dicyclohexylamine (5 ml, slight excess) was added via motor driven syringe over 30 minutes. After the addition was complete,
15 the reaction was stirred an additional 30 minutes. The precipitated dicyclohexylamine hydrochloride was removed by filtration and the acetone filtrate reduced in volume in vacuo until most of the product had precipitated (yield 9.5 g, m.p. 81-82°C).

20

EXAMPLE 6

A. 2-Bromopropionyl substituted polystyrene (Compound 11)

Polystyrene (20 g Dow Styron 678, general purpose) was dissolved in 200 ml methylene chloride followed by 4.58 g (0.025 mol) 2-bromopropionyl chloride. Aluminum
25 chloride (3.65 g, 0.0275 mol) was added portionwise with stirring over 20 minutes at room temperature. The mixture was poured into 600 ml of water containing 25 ml concentrated HCl. The phases were mixed until the methylene chloride became colorless; whereupon the methylene chloride
30 layer was separated and poured slowly in methanol to precipitate the polymeric product, which was redissolved in methylene chloride then reprecipitated in methanol, collected and dried to give 14.5 g of functionalized polymer (% C = 86.1, H = 7.1%, Br = 6.2%; approximately
35 9-10% of the rings are brominated).

B. 2-Octadecanoylpropanoyl substituted polystyrene (Compound 12)

A 6 g portion of 2-bromopropionyl substituted polystyrene (0.0047 mol Br) was dissolved in 30 ml of methylene chloride. Sodium octadecanoate (0.0047 mol) and DMF (30 ml) was added and the reaction was shaken at room temperature for two weeks. Infrared spectral data indicated that ester groups had formed. The reaction mixture was poured into methanol and the precipitated polymer was redissolved (CH_2Cl_2) and precipitated (MeOH) (IR - 1748 cm^{-1} , 1695 cm^{-1}).

EXAMPLE 73'-Methoxybenzoin octadecanoate (Compound 13)

3'-Methoxybenzoin (5 g, 0.021 mol) was dissolved in 200 ml of toluene containing one equivalent of triethylamine. One equivalent of octadecanoyl chloride in 20 ml of toluene was added slowly to the cooled (ice bath) stirred benzoin solution. Stirring was continued with ice bath cooling for one hour. The reaction mixture was then filtered free of precipitated amine salt and the filtrate was evaporated to give an oil which solidified to give a low melting solid. The hexadecanesulfonate (Compound 14) and perfluorooctanoate (Compound 15) (m.p. 55-58°C) esters were similarly prepared from the corresponding acid chlorides.

EXAMPLE 84,5-Dimethoxyl-2-nitrobenzyl octadecanoate (Compound 16)

To a stirred mixture of 4,5-dimethoxy-2-nitrobenzyl alcohol (2.13 g, 0.01 mol) and 1.4 ml of triethylamine in 75 ml of methylene chloride at 5°C, octadecanoyl chloride (3.33 g, 0.01 mol) was added dropwise over 1.5 hours. The mixture was stirred overnight at room temperature. The homogeneous solution which was obtained was washed with saturated NaHCO_3 followed by water. The methylene chloride layer was dried over Na_2SO_4 and evaporated in vacuo to give a solid which was crystallized from ether-hexane to give 2.5 g of ester (m.p. 87-89°C).

EXAMPLE 94,5-Dimethoxy-2-nitrobenzyl perfluorooctanoate (Compound 17)

In 100 ml of toluene 4,5-dimethoxy-2-nitrobenzyl alcohol (2.13 g, 0.01 mol) and 1.4 ml of triethylamine were
5 mixed. Perfluorooctanoyl chloride (4.33 g, 0.01 mol) was added dropwise to the stirred toluene solution. The reaction mixture was stirred an additional 30 minutes after the completion of the addition and then extracted with saturated NaHCO_3 and then water. The organic layer was
10 dried over Na_2SO_4 and evaporated in vacuo to give an oil which solidified on overnight storage at 0-2°C. The solid was crystallized from ether-hexane (m.p. 65-66°). 4,5-Methylenedioxy-2-nitrobenzyl perfluorooctanoate (Compound 18) was similarly prepared from 4,5-methylenedioxy-2-
15 nitrobenzyl alcohol (m.p. 70-71°C).

EXAMPLE 10N-Octadecyl-0-(2-nitrobenzyl)carbamate (Compound 19)

A mixture of 7.7 g (0.03 mol) of octadecylisocyanate and 4.6 g (0.03 mol) 2-nitrobenzyl alcohol in
20 100 ml of toluene was refluxed for five days. On cooling, a solid precipitated which was filtered and washed with toluene to give 8.0 g (m.p. 84-85°C) of the carbamate.

EXAMPLE 11Bis(2-Nitrobenzyl ester) of 9-octadecenoic

25 acid dimer (EMPOL 1010) (Compound 20)

The bis acid chloride of 9-octadecenoic acid dimer was prepared from the acid dimer ("EMPOL" 1010)* with thionyl chloride in toluene. To a solution of 15.3 g (0.1 mol) 2-nitrobenzyl alcohol and 10.1 g (0.1 mol) triethylamine in 100 ml of benzene was added slowly under
30 N_2 30.0 g (0.05 mol) of the acid chloride with stirring. The reaction was stirred one hour at room temperature after the addition had been complete. The precipitated triethyl ammonium chloride was removed by filtration and
35 the filtrate evaporated to dryness to give the diester.

*Footnotes 1-10 are identified following Example 83.

EXAMPLE 12N-Octadecanoyl-8-nitro-1,2,3,4-tetrahydroquinoline (Compound 21)

8-Nitro-1,2,3,4-tetrahydroquinoline (1.8 g, 0.01 mol) was refluxed in 200 ml xylene with excess octadecanoyl chloride for ten days. The solvent was then evaporated in vacuo and the residue which remained was dissolved in ethanol. The ethanol was then evaporated in vacuo and the ethyl octadecanoate formed from the excess acid chloride was taken up in cold hexane and the product was isolated by filtration and crystallized from hexane (2.5 g, m.p. 61°C).

PHOTOLABILE BLOCKED SURFACTANT COMPOSITIONSEXAMPLES 13-16

A series of coating solutions were prepared in methylethylketone to contain 30% by weight of "Carboset" 525² (a carboxy functionalized acrylic resin available from B. F. Goodrich Company) and 2-nitrobenzyl perfluorooctanoate (Compound 1) at various weight percentages based on solids. The solutions were coated onto strips of copper foil using a #8 wire wound coating rod (R.D. Specialties Company). The coated samples (coating thickness was about 20 μ m) were allowed to air dry one hour. A portion of each sample was irradiated with a General Electric H3T7 medium pressure mercury lamp for the times and at the distances noted in Table I. The irradiated samples were laminated with "Scotch" Brand "Magic Mending" Tape (available from the 3M Company) and the tape then peeled at a 180° angle from the sample. The mode of adhesive failure for each was observed and indicated in Table I.

It is apparent from the data in Table I that carboxy functionalized acrylic resin containing from more than 1% to less than 10% of photolabile blocked surfactant (Compound 19) adheres well to copper foil until it has been irradiated, whereon it is readily removed from the copper foil.

TABLE I

Ex. No.	% Compound 1	Radiation (Time/Distance)	Peel Result ^(a)
13	1.0	0 min	NR
13	1.0	9 min/2.5 cm	NR
13	1.0	20 min/10 cm	NR
14	2.0	0 min	NR
14	2.0	3 min/2.5 cm	R
14	2.0	15 min/10 cm	R
15	5.0	0 min	NR
15	5.0	2 min/2.5 cm	R
15	5.0	10 min/10 cm	R
16	10.0	0 min	R

(a) "R" indicates that release of the coating from the substrate copper occurred and "NR" indicates that release of the coating from the substrate did not occur. In other tables "R/NR" indicates that there was only partial release of the coating from the substrate.

EXAMPLES 17-22

Examples 17-22 illustrate the inoperability of photolabile blocked compounds that are not sufficiently surfactant.

Samples of "Carboset" 525² (20% methylethylketone) containing 5 and 10 weight percent of 2-nitrobenzyl trifluoro-acetate based on total solids were coated with a #50 coating rod onto Parker "Bonderite" #40³ steel panels. Portions of the dried, coated samples were irradiated with the GE H3T7 lamp for up to 30 minutes at 5 cm distance. Pressure sensitive adhesive tape (#610 available from the 3M Company) was applied to each portion and peeled off at a 180° angle. The resin-metal adhesion showed failure at the tape-resin interface. No photorelease was observed. The identical result (no photorelease) was obtained when the perfluorobutanoate and perfluorohexanoate esters of 2-nitrobenzyl alcohol were used in place of 2-nitrobenzyl trifluoroacetate.

EXAMPLE 23

A solution containing 10% by weight of a high molecular weight poly(methyl methacrylate) available under the trade designation "Elvacite" 2041 from DuPont and 6% by weight of 2-nitrobenzyl perfluorooctanoate (Compound 1) based on total solids was coated onto copper foil using a #26 coating rod. The sample was dried and irradiated for three minutes with a GE H3T7 lamp at 2.5 cm. Pressure sensitive tape, laminated to the coating and peeled off, easily removed the coating from the copper foil in irradiated areas.

EXAMPLES 24-27

To a solvent solution containing 38.2% by weight of safflower alkyd modified polyurethane resin, sold under the trade designation "EPIC" varnish by the Enterprise Paint Company of Wheeling, Ill. was added sufficient 2-nitrobenzyl perfluorooctanoate to provide 5% and 10% by weight of octanoate based on total solids. Portions of the mixture were brush coated onto Parker "Bonderite" #40³ steel test panels and onto copper foil strips. The coatings were allowed to dry for 16 hours. Samples were then irradiated for three minutes using the output of a GE H3T7 lamp at a distance of 2.5 cm. Pressure sensitive adhesive tape (#610 sold by the 3M Company) was laminated to each sample and peeled off at 180°. The varnish cleanly delaminated from the steel panels and copper strips in exposed areas but not in unexposed areas.

EXAMPLES 28-31

Examples 24-27 were repeated using sufficient 2-nitrobenzyl hexadecanesulfonate (Compound 9) to provide the varnish with 4% by weight of the photolabile sulfonate based on total solids. The varnish cleanly delaminated from metal strips in exposed samples but not from unexposed samples. When the examples were repeated using varnish with 5% by weight of 2-nitrobenzyl hexadecanesulfonate (Compound 9) adhesion of the coating was poor even in the absence of irradiation.

EXAMPLES 32-35

A series of coating solutions were prepared in methylethylketone to contain 20% by weight of "Carboset" 5252. and α -methylphenacyl perfluorooctanoate (Compound 2) at various weight percentages based on total solids. The solutions were coated onto Parker "Bonderite" #40³ steel panels and copper foil using a #50 coating rod and air dried overnight. Samples of the coatings were irradiated as noted in Table II and the coating tested for adhesion by peeling a laminated #610 (sold by the 3M Company) pressure sensitive adhesive tape from the coating as is described in Examples 13-16.

Data presented in Table II shows that the coating compositions of "Carboset" 5252. are readily photoreleased from copper substrates when there is present about 2% of photolabile blocked surfactant Compound 2 and from steel when there is present about 3% of Compound 2.

TABLE II

	Ex. No.	% Compound 2	Radiation (Min. at 2.5 cm)	Peel Results ^(b)	
				On Steel	On Copper
20	32	1.0	0	NR	
	32	1.0	1	NR	
	32	1.0	3	NR	
	32	1.0	7	NR	
25	32	1.0	10	NR	
	33	2.0	0	NR	
	33	2.0	1	NR	
	33	2.0	2	NR	R
	33	2.0	3	NR	
30	34	3.0	0	NR	
	34	3.0	1	R/NR	
	34	3.0	2	R	R
	34	3.0	3	R	
	35	5.0	0	NR	
35	35	5.0	0.25	R/NR	
	35	5.0	0.5	R	
	35	5.0	1	R	R

(b) R and NR are defined in footnote to Table I

EXAMPLES 36-40

Examples 32-35 were repeated using in place of Compound 2 as photolabile blocked surfactant the tetradeca-, hexadeca-, heptadeca-, octadecanoate and 9-octadecenoate esters of 2-nitrobenzyl alcohol (Compounds 5, 6, 7, 4 and 8, respectively). Compound 5 did not provide photorelease. Compounds 6, 7, 4 and 8 provided photorelease of coatings at concentrations above about 3% by weight in "Carboset" 525². At concentrations above about 10%, release occurred without irradiation for Compounds 6, 7, 4 and 8.

EXAMPLE 41

A coating was prepared as described in Examples 32-35 to contain 5% by weight of N-(2-nitrobenzyl)octadecylamine (Compound 23) in "Carboset" 525². After irradiation of the coating for three minutes at a distance of 2.5 cm from a GE H3T7 lamp, the coating was readily peeled from steel by #610 adhesive tape (sold by the 3M Company).

EXAMPLE 42

A solution of poly(90/10:isooctyl acrylate/acrylic acid) pressure sensitive adhesive (30% in heptane-isopropanol) was mixed with enough 2-nitrobenzyl heptadecanoate (Compound 7) to form a solution having 5% by weight of the heptadecanoate ester in the adhesive solids. The adhesive was knife coated at 50 μ m orifice onto 50 μ m polyester film and allowed to air dry. The sample was cut into strips and laminated onto Parker "Bonderite" #40³ steel panels. Portions of the laminated construction were irradiated for five minutes at a distance of 2.5 cm from a GE H3T7 lamp. When the polyester strips were peeled at a 180° angle, the adhesive was cleanly removed along with the polyester from the steel panel in irradiated areas. In the unirradiated areas, adhesive adhered to the metal panel. In the absence of the heptadecanoate additive, adhesive adhered to the steel surface and transferred to the steel surface in both irradiated and unirradiated areas.

A sample of the above adhesive coated polyester was laminated onto aluminum which had been anodized and

silicated. A six minute irradiation with a GE H3T7 lamp at 2.5 cm was enough to allow the polyester film and adhesive to be cleanly removed from the irradiated areas. In unirradiated areas of the sample, adhesive adhered to the aluminum panel on peeling off the polyester film.

EXAMPLE 43

Samples of aluminum which had been anodized and silicated were coated with 20% by weight solution in methylethylketone of "Carboset" 5252² containing 5% and 10% by weight based on solids of 2-nitrobenzyl perfluorooctanoate (Compound 1) and dried. The coatings adhered firmly to the aluminum, however, after irradiation at a distance of 2.5 cm. from a GE H3T7 lamp for five minutes of the coating containing 5% Compound 1 and three minutes of the coating containing 10% Compound 1, the coating was easily removed by peeling off a pressure sensitive tape that had been pressed onto the coatings.

EXAMPLE 44

"Carboset" 5252² coatings containing 3% by weight of N-octadecanoyl-8-nitro-1,2,3,4-tetrahydroquinoline (Compound 21) on "Bonderite" #40³ steel panels were prepared as described in Examples 32-35. The coatings could not be removed by peeling a pressure sensitive tape laminated to their surfaces. After irradiation for three minutes at a distance of 2.5 cm from a GE H3T7 lamp, the coating was easily removed by peeling off a pressure sensitive tape that had been pressed onto the coatings.

EXAMPLES 45-58

To separate portions of a 25% by weight solution of poly(90/10 iso-octyl acrylate/acrylic acid) pressure sensitive adhesive in heptane-isopropanol was added sufficient 2-nitrobenzyl octadecanoate (Compound 4), 2-nitrobenzyl perfluorooctanoate (Compound 1), and 2-nitrobenzyl hexadecanesulfonate (Compound 9) to provide compositions containing 5% to 10% by weight based on total solids of each. Each solution was knife coated onto cellulose acetate film (100 μ m thickness) at an orifice of 75 μ m and allowed to dry three hours. The adhesive coated films were then cut into 1.25 cm strips and laminated adhesive-side

down to "Bonderite" #40³. steel panels and to anodized silicated aluminum. Strong bonding was assured by placing the samples under 1 kg weights for about 16 hours. Samples of each were exposed to the radiation from a GE H3T7 lamp at a distance of 5 cm for the times shown in Table III and the tapes peeled from the metal substrates.

Data presented in Table III shows that pressure sensitive adhesives containing a photolabile blocked surfactant of the invention are readily releasable from steel or aluminum after illumination by ultraviolet light, but are not without the illumination. Blocked surfactant Compounds 4 and 9 provide ready release of adhesives from steel and aluminum at concentrations of from 5% or less to 10% or more. Blocked surfactant Compound 1 was effective on steel at concentrations of 5% or less; but on aluminum, more than 5% was needed to provide release on irradiation.

TABLE III

Ex. No.	Compound		Radiation (Min. at 5 cm)	Peel Results ^(c)	
	No.	% Conc.		On Steel	On Alum.
5	45	-	0	NR	NR
	45	-	5	NR	NR
	45c	-	10	NR	NR
	46a	4	5	NR	NR
	46	4	5	R/NR	NR
10	46	4	10	R	R/NR
	46	4	0	NR	NR
	46	4	5	R	R
	46	8	10	R	R
	47	1	5	NR	NR
15	47	1	5	R/NR	NR
	47	1	5	R	NR
	47	1	10	R/NR	NR
	47	1	10	R	NR
	47	1	10	R	R/NR
20	48	9	5	NR	NR ^(e)
	48	9	5	R	R ^(e)
	48	9	10	R	R ^(e)
	48	9	10	phase separation ^(d)	

(c) R, NR and R/NR are defined in (a) following Table I.

(d) Compound 2 is not soluble in the adhesive at this concentration

(e) Similar results are obtained when Ex. 48 was repeated using, in place of isooctyl acrylate/acrylic acid, the adhesive 90/10-(2-methylbutyl acrylate/acrylic acid), and, in place of aluminum, an enameled aluminum as substrate.

TABLE IV

	Ex. No.	% Compound 9	Substrate	Radiation (Min. at 5 cm)	Peel Force (g/1.25 cm)
5	51a	2.5	#40 steel	0	312
	51b	2.5	"	3	312
	51c	2.5	"	6	113
	52a	4	"	0	170
	52b	4	"	4	113
10	53a	5	"	5	85
	54a	5	Aluminum	0	340
	54b	5	"	5	85
	55a	5	Silicon	0	340
	55b	5	"	5	85

EXAMPLE 56

15 A solution of "Carboset" 525². containing 5% relative weight solids of Compound 20 the bis-2-nitrobenzyl ester of "oleic acid dimer" ("EMPOL" 1010¹.), was coated with a #50 coating rod onto a "Bonderite" #40³. steel panel and allowed to dry overnight. The panel was irradiated for
20 five minutes at 2.5 cm with a GE H3T7 lamp. The carboset film easily delaminated from the steel panel in the irradiated areas, yet held fast to the steel in the unexposed portion of the panel.

EXAMPLE 57

25 A solution of "Elvacite" 2044⁷. containing 3% relative weight solids of N-octadecyl-O-(2-nitrobenzyl)carbamate (Compound 19) in methylethylketone was coated onto a "Bonderite" #40³. steel panel and allowed to air dry. After
30 five minutes irradiation of the film at 2.5 cm distance from a GE H3T7 lamp, the "Elvacite" film was easily delaminated from the surface of the steel panel in the exposed areas.

EXAMPLES 58-59

35 Two solutions, one containing 20% "Carboset" 525². in methylethylketone and 0.5% relative of solids of 2-nitrobenzyl hexadecanesulfonate (Compound 9), and the other containing 20% "Elvacite" 2044⁷. in methylethylketone and 1.5% relative weight solids of N-octadecyl-O-(2-nitrobenzyl)carbamate (Compound 19), were each repetitively

coated onto two "Bonderite" #40³. steel panels to give coatings about 0.25 mm dry thickness. After five minutes irradiation at 2.5 cm distance from a GE H3T7 lamp, the films were easily stripped from the steel panel by grasping an edge of the film and peeling.

EXAMPLE 60

An adhesive tape was prepared from a 90/10 isooctylacrylate/acrylamide adhesive in ethylacetate-toluene containing 8% relative weight solids of 2-nitrobenzyl hexadecanesulfonate (Compound 9) by knife coating an adhesive solution onto polyester film. The dried tape was laminated onto a polyester film that had been primed with a coating of aluminum oxide. A portion of the tape was irradiated with a GE H3T7 lamp for five minutes at 2.5 cm. The peel strength of the tape was roughly measured with a spring scale at 180° peel angle to compare irradiated with unirradiated laminates. Peel adhesion of irradiated tapes using a peel rate of about 3.5 cm/sec was about 0 g/1.25 cm; peel adhesion of unirradiated tapes was about 425 g/1.25 cm accompanied by some adhesive transfer to the aluminum oxide surface.

EXAMPLES 61-65

Samples of "Carboset" 525². (20% in methylethylketone) containing 5% and 10% relative weight solids of 3'-methoxybenzoin octadecanoate (Compound 13) were coated onto a "Bonderite" #40³. steel panel with a #40 coating rod. The dried samples were irradiated for the noted times with a GE H3T7 lamp at 2.5 cm and were tested for photorelease of the "Carboset" 525². film.

TABLE V

Ex. No.	%Compound 13	Radiation (Min. at 2.5 cm)	Peel Results ⁽¹⁾ on Steel
61	5	0	NR
62	5	≤ 20	NR
63	10	0	NR
64	10	2.5	NR
65	10	5	R

(1) R and NR are defined in (a) following Table I.

EXAMPLES 66-70

Samples of "Carboset" 525². (20% methylethylketone) containing the concentrations based on solids of 3'-methoxybenzoin perfluorooctanoate (Compound 15) and hexadecanesulfonate (Compound 14) indicated in Table VI were coated onto "Bonderite" #40³ steel test panels with a #40 coating rod and allowed to air dry one hour. The samples were irradiated with a GE H3T7 lamp at 5 cm for the times noted and then examined for photorelease of the "Carboset" 525². film from the test panel.

TABLE VI

Ex. No.	Compound No.	%	Radiation (Min. at 5 cm)	Peel Results ⁽¹⁾ on Steel
66a	15	1	0	NR
66b	15	1	≤ 5	NR
67a	15	3	0	NR
67b	15	3	3	R
68	15	5	0	R
69a	14	1	0	NR
69b	14	1	1	NR
69c	14	1	3	R
70a	14	5	0	R

(1) R and NR are defined in (a) following Table I.

EXAMPLES 71-74

Adhesive tape constructions were prepared from 90/10 iso-octylacrylate/acrylic acid adhesive solution (heptane-isopropanol) containing 3% and 5% relative weight solids of 3'-methoxybenzoin hexadecanesulfonate (Compound 14). The solutions were knife coated at a 50 μm orifice onto 75 μm polyester film. The samples were air dried one hour, cut into one inch strips and laminated with heat and rubber roller pressure onto anodized-silicated aluminum. Samples of each were irradiated five minutes at 5 cm distance from a GE H3T7 lamp. The peel adhesion of unirradiated and irradiated samples was measured with a spring scale as described in Examples 51-55. At both concentrations, the peel force dropped from about 595 g/1.25 cm for the unirradiated samples to about 155 g/1.25

cm for the irradiated samples.

EXAMPLES 75-76

Adhesive tape constructions were prepared as follows: [75] 4.0 g of a 90/10 iso-octylacrylate/acrylic acid adhesive (25% in heptane-isopropanol) were mixed with 0.03 g 2-nitrobenzyl hexadecanesulfonate (Compound 9) in 4.0 g of methylethylketone, and [76] 4.0 g of a 95/5 iso-octylacrylate/acrylic acid adhesive (25% in heptane-isopropanol) were mixed with 0.03 g 2-nitrobenzyl hexadecanesulfonate in 4.0 g of methylethylketone. The solutions were coated with a #18 coating rod onto polycarbodiimide primed polypropylene film. The samples were air dried overnight and cut into 1.25 cm strips. The strips were pressure laminated with four passes from a rubber roller onto anodized-silicated aluminum sheet. The samples were exposed to the radiation from a GE H3T7 lamp at a distance of 5 cm for the times indicated in Table VII. The force required to peel each tape sample from the aluminum was measured using a peel rate of about 3.5 cm/sec.

TABLE VII

	Radiation (Min. at 5 cm)	Peel Force	
		Ex. 75 (g/1.25 cm)	Ex. 76 (g/1.25 cm)
	0	1930	2150
25	0.5	1080	170
	1	850	110
	2	450	140
	3	450	85

EXAMPLE 77

Super-calendered, semi-bleached 62 lb. Kraft paper (available from Thilmany Company) was coated using a #26 coating rod with: (a) 20% solution in methylethylketone of "Carboset" 525² containing 1.5% by weight of 2-nitrobenzyl hexadecanesulfonate (Compound 9), (b) 10% solution in methylethylketone of "Carboset" 525² containing 3% Compound 9, (c) 10% solution in methylethylketone of "Estane" 5715⁸ containing 2% Compound 9, and (d) 10% solution in methylethylketone of "Elvacite" 2044⁷ containing 5% Compound 9. Each coating was dried and exposed for

three to five minutes to the radiation from a GE H3T7 lamp at a distance of 2.5 cm. The coated samples were then laminated with #610 pressure sensitive tape (sold by the 3M Company) and the tape peeled off at a 180° angle. In irradiated areas, the resin coating was cleanly removed from the paper but remained adhered to the sized paper in unexposed areas.

EXAMPLES 78-80

A sample of a 90/10 2-methylbutylacrylate/acrylic acid (14 g of a 25% solution in acetone-heptane) adhesive solution containing 0.07 g of 4,5-dimethoxy-2-nitrobenzyl hexadecanesulfonate (Compound 10) was knife coated at a 375 μ m orifice onto 25 μ m polyester film. The sample was allowed to air dry and was cut into strips which were laminated onto anodized aluminum, epoxy printed circuit board material, and glass slides with a hand roller. The samples were half-covered and irradiated with a GE H3T7 lamp at 10 cm for five minutes. The strips were peeled from the substrate and the mode of adhesive failure noted: R = photorelease or clean removal of adhesive from the substrate; NR = adhesive transfer from the polyester film to the substrate.

TABLE VIII

	Substrate	Irradiation Time (Min. at 10 cm)	Peel Results (1)
25	Al	0	NR
	Al	5	R
	Epoxy	0	NR
	Epoxy	5	R
30	Glass	0	NR
	Glass	5	R

(1) R and NR are defined in (a) following Table I

Similar results are obtained when 4,5-methylene-dioxy-2-nitrobenzyl hexadecanesulfonate is substituted for Compound 10. When a 90/10 iso-octylacrylate/acrylic acid adhesive is used in place of 2-methylbutyl acrylate/acrylic acid adhesive, similar results were obtained for the glass slide and aluminum substrates; however, little photorelease effect was observed for the epoxy substrate.

EXAMPLE 81

A solution of "Carboset" 525². (20% in methylketone) containing 3% relative weight solids of 4,5-dimethoxy-2-nitrobenzyl hexadecanesulfonate (Compound 10) was coated onto a sample of a gold vapor deposited layer on polyester film with a #26 coating rod. The dried sample was irradiated with a Beskey Ascor 2 kw photopolymer medium pressure mercury bulb through glass at 45 cm for three minutes. In the irradiated areas, the "Carboset" 525². film could easily be peeled from the gold surface. In the unexposed areas, the "Carboset" 525². film remained tightly adhered to the gold layer.

EXAMPLE 82

A sample of 15 g of a 15% solution of "Vinac" ASB 516⁹. (Air Products Company vinylacetate resin) in methyl-ethylketone and a solution of 0.07 g of 4,5-dimethoxy-2-nitrobenzyl hexadecanesulfonate (Compound 10) in 0.2 ml of methylene chloride were mixed and knife coated at a 75 μ m orifice onto a sample of vapor coated aluminum (500 Å thick) on 75 μ m polyester. The sample was allowed to air dry 30 minutes and was irradiated with a Beskey Ascor 2 kw photopolymer lamp at 45 cm through glass for 90 seconds. In the irradiated areas the "VINAC" film⁹. was cleanly removed from the aluminum surface. In unirradiated samples, the "VINAC" film⁹. adhered tightly to the aluminum.

An identical result was obtained when a polyester resin, Goodyear "Vitel" PE-222¹⁰. (15% in methylethylketone), was substituted for the "VINAC" ASB 516⁹. resin. The "Vitel"¹⁰. resin could also be made to photorelease from the surface of vapor coated nickel on polyester using the above procedure and three minutes of irradiation.

EXAMPLE 83

A sample of "Vitel" PE-222¹⁰. resin (15% in methyl-ethylketone) containing 3% relative weight solids of 4,5-dimethoxy-2-nitrobenzyl hexadecanesulfonate (Compound 10) was coated with a #38 coating rod onto 75 μ m polyester film which had been primed by exposure to a corona discharge. The dried sample was irradiated for three minutes with a Beskey Ascor 2 kw photopolymer lamp at 45 cm. The irradi-

ated "Vitel"¹⁰. resin was easily peeled from the corona primed polyester film. Unirradiated areas adhered tightly. When the procedure was repeated for unprimed samples of polyester film, the "Vitel"¹⁰. resin adhered tightly in both irradiated and unirradiated areas.

EXAMPLE 84

Preparation of 8-Nitrocinnamyl Alcohol

Benzaldehyde (10.6 g, 0.1 mol) and 2-nitroethanol (9.1 g, 0.1 mol) were dissolved in 25 ml of methanol. The mixture was cooled in an ice bath and 10 ml of 10.5 M aqueous sodium hydroxide was added dropwise with stirring at such a rate that the temperature of the reaction was maintained below 15°C. As the addition progressed a white precipitate separated. Water (70 ml) was added 15 minutes after completion of the addition and the reaction was poured into 50 ml of 4.8 M hydrochloric acid. The oil product was separated from the aqueous (upper) layer by decanting and the product was taken up in ether. The ether solution was washed three times with sodium bisulfite solution to remove any unreacted benzaldehyde. The ether layer was dried and evaporated in vacuo to yield the product as an oil.

EXAMPLE 85

Preparation of 8-Nitrocinnamyl Perfluorooctanoate

8-Nitrocinnamyl alcohol (5.4 g, 0.03 mol) and one equivalent of triethylamine (3.03 g, 0.03 mol) were dissolved in 100 ml of toluene. The solution was cooled in an ice bath and perfluorooctanoyl chloride (12.6 g, 0.03 mol) was added dropwise with stirring. The reaction was stirred an additional two hours and diluted with ether. The reaction was extracted with water and the organic layer was dried over anhydrous magnesium sulfate and evaporated in vacuo. The oily product was crystallized from petroleum ether to give yellow prisms, mp 79-81°, IR 1785, 1655, 1535, 1325, and 1200 cm^{-1} . A solution of the material in 95% ethanol showed an absorption of λ_{max} at 302 nm, epsilon = 10,800 which rapidly decreased exposure to the GE H3T7 source. This loss of the 302 nm absorption was accompanied by a decrease in the pH (increased acidity) of the solution as

as indicated by methyl red pH indicator.

EXAMPLE 86

β -Nitrocinnamyl perfluorooctanoate as a photolabile blocked surfactant

A sample of 0.01 g of β -nitrocinnamyl perfluorooctanoate was dissolved in a 20% solution of "Carboset" 525² in methylethylketone. The mixture was coated onto a "Bonderite"³ #40 steel panel with a #8 coating rod. The air dried sample (overnight at 20°C) was partially covered and irradiated with a GE H3T7 source at a distance of 5 cm for 5 minutes. Adhesive tape (#610 available from the 3M Company) was applied to the scored resin surface and peeled. The resin released from the metal surface only in the exposed area.

Footnotes

1. "EMPOL" 1010 is the trade designation of Emery Industries, Inc. for 9-octadecenoic acid dimer.
2. "Carboset" 525 is the trade designation of the B.F. Goodrich Company for a carboxy functionalized acrylic resin.
3. "Bonderite" #40 is the trade designation of the Oxy-Metal Industries Corporation, Parker Division for a phosphate surface treatment for unpolished cold rolled steel test panels.
4. "Elvacite" 2041 is the trade designation of the DuPont Company for a high molecular weight poly(methyl methacrylate).
5. "EPIC" varnish is the trade designation of the Enterprise Paint Company of Wheeling, Ill. for a solvent solution containing 38.2% by weight of safflower alkyd modified polyurethane resin.
6. "Styron" 678 is the trade designation of the Dow Chemical Company for a general purpose polystyrene.
7. "Elvacite" 2044 is the trade designation of the DuPont Company for medium molecular weight poly(n-butylmethacrylate).
8. "Estane" 5715 is the trade designation of the B.F. Goodrich Company for a polyurethane elastomer.
9. "VINAC" ABS 516 is the trade designation of the Air Products Company for a vinylacetate resin.
10. "Vitel" PE-222 is the trade designation of the Goodyear Tire and Rubber Company for a linear saturated polyester resin.

Claims

1. A compound characterized by the feature of being a photolabile blocked surfactant compound having the general formula $(P-X)_a R$ wherein

5 $(-X)_a R$ is the hydrogen-eliminated residue of a surfactant having the formula $(H-X)_a R$ wherein X is a polar divalent radical;

P is a photolabile masking group which prior to exposure to actinic radiation masks the polar properties of X and upon exposure to actinic radiation will unmask the polar properties of X;

R is a hydrophobic group which provides in said surfactant $(H-X)_a R$ a log (critical micelle concentration) equal to or less than -2; and

15 a is a number from 1 to 4 to satisfy the valency of R.

2. The photolabile blocked surfactant compound of claim 1 further characterized by X being selected from the

group consisting of $-OC(=O)-$, $-OS(=O)-$, and $-N(R^1)-$ wherein R^1

20 is hydrogen or lower alkyl having from 1 to 4 carbon atoms.

3. The photolabile blocked surfactant of claim 1 further characterized by R being selected from:

(a) R^2-

25 (b) $R^3-C(=O)-CH_2CH_2-$

(c) $R^3-C(=O)-N(R^1)(CH_2)_n-$

(d) $R^4-O-C(=O)-CH_2CH(R^4)-C(=O)-R^4$

wherein R^2 is

- (1) straight chain alkyl, alkenyl, alkynyl, or alkylphenyl group having 12 to 30 carbon

atoms when X is $\begin{array}{c} \text{O} \\ \parallel \\ -\text{OS}- \\ \parallel \\ \text{O} \end{array}$;

- 5 (2) straight chain alkyl, alkenyl, alkynyl, or alkylphenyl group having 15 to 30 carbon

atoms when X is $\begin{array}{c} \text{O} \\ \parallel \\ -\text{OC}- \end{array}$ or $\begin{array}{c} \text{O} \\ \parallel \\ -\text{N}- \\ | \\ \text{R}^1 \end{array}$ in which R¹

is defined above; or

- (3) a perfluoroalkyl, alkenyl, or -alkynyl group having 7 to 30 carbon atoms;

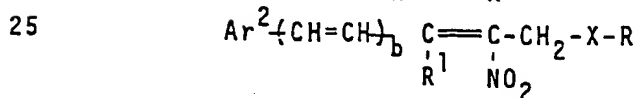
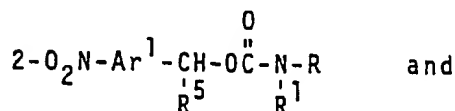
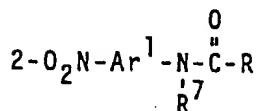
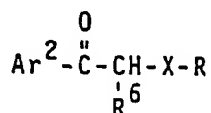
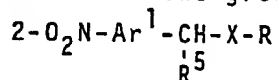
10 R³ is a straight chain alkyl, alkenyl, alkynyl, or alkylphenyl group having 11 to 30 carbon atoms or a perfluoroalkyl group having 7 to 30 carbon atoms;

R⁴ is a straight chain alkyl, alkenyl, alkynyl, alkylphenyl or perfluoroalkyl, -alkenyl, or -alkynyl group having 7 to 30 carbon atoms; and

n is 1 or 2; and

a is 1.

4. The photolabile blocked surfactant compound of claim 1 further characterized by having a general formula selected from the group consisting of



wherein

Ar¹ is a mononuclear or polynuclear divalent aryl group having 6 to 14 carbon atoms or heteroaromatic group having 5 to 13 carbon atoms with heteroatoms selected from oxygen, nitrogen or sulfur atoms, the nuclei of which may be substituted by one auxochromic or bathromic group;

Ar² is the same as Ar¹ except that Ar² is monovalent;

R⁵ is hydrogen, lower alky, phenyl, phenyl substituted by an auxochromic or bathochromic group as defined for Ar¹, or a lower alkylene group joining CH to Ar and forming a five- or six-membered heterocyclic ring;

R⁶ is phenyl substituted by 3-alkoxy or 3,5-dialkoxy in which the alkyl group can be a hydrogen atom, a lower alkyl group, having from 1-4 carbon atoms, or a phenyl group;

R⁷ is hydrogen, lower alkyl having from 1-4 carbon atoms, or lower alkylene having 2-4 carbon atoms joining N to Ar² forming a 5- or 6-membered heterocyclic ring; and

b is zero or one.

5. A coating composition which is releasable from a substrate upon exposure to actinic radiation comprising an actinic radiation-transmissive thermoplastic organic film-forming binder having blended therein, in a quantity sufficient to release a coating of said binder from a substrate, a compound characterized by being a photolabile blocked surfactant having the general formula $\{P-X\}_2R$ wherein

$\{P-X\}_2R$ is the hydrogen-eliminated residue of a surfactant having the formula $\{H-X\}_2R$ wherein X is a polar divalent radical;

P is a photolabile masking group which prior to exposure to actinic radiation masks the polar properties of X and upon exposure to actinic radiation will unmask the polar properties of X;

5 R is a hydrophobic group which provides in said surfactant $(H-X)_aR$ a log (critical micelle concentration) equal to or less than -2; and

a is a number from 1 to 4 to satisfy the valency of R.

- 10 6. The coating composition of claim 5 wherein the film-forming binder is characterized by being a pressure sensitive adhesive composition.
7. The coating composition of claim 5 wherein said film-forming binder is further characterized by having a
15 molecular weight of at least 10,000.
8. The coating composition of claim 5 wherein said film-forming binder is further characterized by being selected from the group consisting of copolyesters based on an acid selected from terephthalic, iso-
20 phthalic, sebacic, adipic and hexahydrophthalic and mixtures thereof.
9. The coating composition of claim 5 wherein said film-forming binder is further characterized by being selected from the group consisting of alkyd resins
25 based on phthalic anhydride and glycerine.
10. The coating composition of claim 5 wherein said film-forming binder is further characterized by being selected from the group consisting of poly(hexamethyleneadipamide) and polycaprolactam.
- 30 11. The coating composition of claim 5 wherein said film-forming binder is further characterized by being selected from the group consisting of vinyl acetate

5 copolymers, vinylchloride copolymers, vinylidene chloride copolymers, ethylene copolymers, polyacrylates, cellulose esters, polyvinyl acetals, polyurethanes, polycarbonates, styrene-maleic anhydride and maleic acid copolymers.

12. The coating composition of claim 5 wherein said composition is further characterized by also including a compatible solvent.
- 10 13. The coating composition of claim 5 wherein said photolabile blocked surfactant compound is further characterized by containing therein at about 1 to 10 parts per 100 parts of said film-forming binder.
- 15 14. The coating composition of claim 12 further characterized by having a solids concentration of about 10 to 50 parts per 100 parts total composition.
- 20 15. The coating composition of claim 12 further characterized by said solvent being selected from the group consisting of ketones, aromatic hydrocarbons, halocarbons, esters, ethers, dioxane, tetrahydrofuran, nitromethane, nitroethane, and acetonitrile.
16. The coating composition of claim 5 further characterized by also including minor amounts of additives which do not interfere with the releasability of the coating on exposure to radiation.
- 25 17. The coating composition of claim 16 further characterized by said additives being selected from the group consisting of coating aids, wetting agents, ultraviolet absorbers, plasticizers, fillers, pigments, dyes and mixtures thereof.
- 30 18. A substrate characterized by being coated with the coating composition of claim 5.

19. A coating method characterized by applying the coating composition defined in claim 5 to a substrate.

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